Indicative Energy Technology Assessment of Advanced Rechargeable Batteries†

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ABSTRACT

Several 'Advanced Rechargeable Battery Technologies' (ARBT) have been evaluated in terms of various energy, environmental, economic, and technical criteria. Their suitability for different applications, such as electric vehicles (EV), consumer electronics, load levelling, and stationary power storage, have also been examined. In order to gain a sense of perspective regarding the performance of the ARBT [including Lithium-Ion batteries (LIB), Li-Ion Polymer (LIP) and Sodium Nickel Chloride (NaNiCl) {or 'ZEBRA'} batteries] they are compared to more mature Nickel-Cadmium (Ni-Cd) batteries. LIBs currently dominate the rechargeable battery market, and are likely to continue to do so in the short term in view of their excellent all-round performance and firm grip on the consumer electronics market. However, in view of the competition from Li-Ion Polymer their long-term future is uncertain. The high charge/discharge cycle life of Li-Ion batteries means that their use may grow in the electric vehicle (EV) sector, and to a lesser extent in load levelling, if safety concerns are overcome and costs fall significantly. LIP batteries exhibited attractive values of gravimetric energy density, volumetric energy density, and power density. Consequently, they are likely to dominate the consumer electronics market in the long-term, once mass production has become established, but may struggle to break into other sectors unless their charge/discharge cycle life and cost are improved significantly. ZEBRA batteries are presently one of the technologies of choice for EV development work. Nevertheless, compared to other ARBT, such batteries only represents an incremental step forward in terms of energy and environmental performance.

KEYWORDS: energy storage, rechargeable batteries, technology assessment, economics, environment

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1. INTRODUCTION

1.1 Background

Energy systems pervade industrial societies whilst providing heat and power for human development. But they also put at risk the quality and longer-term viability of the biosphere as a result of unwanted, 'second order' effects [1]. Arguably the principle environmental side-effect of energy supply is the prospect of global warming due to an enhanced 'greenhouse effect' induced by combustion-generated pollutants [1,2]. The most recent (2013) scientific assessment by the *Intergovernmental Panel on Climate Change* (IPCC) states that "it is extremely likely that human influence has been the dominant cause of the observed warming since the mid-20th Century" [2]. They argue that 'greenhouse gas' (GHG) emissions from human activities trap long-wave thermal radiation from the earth's surface in the atmosphere (not strictly a 'greenhouse' phenomena), and that these are the main cause of rises in climatic temperatures. The IPCC believe that the evidence for anthropogenic climate change has grown since their previous science report in 2007 "thanks to more and better observations, an improved understanding of the climate system response and improved climate models" [2]. Carbon dioxide (CO_2; the main GHG) is thought to have a 'residence time' in the atmosphere of around one hundred years [1,3]. There is consequently a worldwide need to cut down GHG emissions by more than 80% in order to stabilize the climate change at a moderate 2^{o}C temperature rise by 2050 [4]. This implies major changes in the way in which energy is sourced, generated and consumed in the UK over the coming four decades. Alongside the negative environmental 'side-effects' of heat and power generation there remain concerns about the security of energy supplies into some industrialised countries. The depletion of fossil fuel resources also presents a challenge, particularly in regions dependent upon conventional sources of fossil fuels**.**

Achieving a carbon reduction target of 80% by 2050 will mean a transition in the systems for producing, delivering and using energy that is not only low carbon, but also secure and affordable, thus resolving the energy policy '*trilemma*' [5]. A portfolio of energy options [5,6] will be required to meet this *trilemma*: energy demand reduction and energy efficiency improvements, carbon capture and storage (CCS) from fossil fuel power plants, and a switch to other low or zero carbon energy sources [various sorts of renewable energy technologies (including wind power, solar photovoltaic arrays, and bioenergy) or nuclear power]. Energy storage devices, such as batteries, will inevitably be required as a means of storing the power generated by 'intermittent' renewable energy sources, such as wind power. In addition, the possibility of introducing battery-powered electric vehicles to replace combustion engine vehicles has also been the subject of serious research effort over recent decades [7-10]. Earlier rechargeable batteries, such as the mature 'lead-acid' battery chemistry, were found to be too bulky and heavy to adequately fulfil either of these roles. Consequently, researchers began investigating alternative battery chemistries that might be more compact and lightweight.

1.2 Batteries as Energy Storage Devices

An electrochemical cell (hereinafter referred to as simply a 'cell') is able to store energy by exploiting the chemical potential difference between its electrodes. A battery consists of a

series of cells in series and or parallel. The main components of a cell are: a metal cathode (or negative electrode), a non-metal anode (or positive electrode), and an ionically conductive material (the 'electrolyte'). A cell generates an electric current during discharge by moving to a more stable state through a set of ionic chemical reactions that occur at the surfaces of the electrodes. Positive ions are formed at the negative electrode as metal atoms 'give up' at least one electron. They then flow towards the anode before reacting with this non-metal positive electrode. In order to maintain the principle of electro-neutrality there must also be a flow of electrons (and thus a current) from the cathode to the anode. This process continues until the negative electrode material is exhausted. Primary cells obviously become redundant at this life-cycle stage, whilst secondary (or 'rechargeable') cells can be recharged. The electrolyte is an essential component of an electrochemical cell, since it facilitates the chemical reactions whilst simultaneously preventing a short circuit. This is achieved by producing the electrolyte from a material that conducts ions, but not electrons, thus ensuring the electrons travel through the external circuit and deliver a current to the load [6,7].

'Advanced Rechargeable Battery Technologies' (ARBT) can be characterized as having higher cell voltages and higher energy densities compared to more mature technologies, such as Nickel-Cadmium (Ni-Cd). Research into this new breed of batteries only began 40 years ago [8-11]. One of the factors driving their recent development has been consumer demand for portable electronic equipment, such as mobile phones, mp3 players, tablets, and laptop computers [9,8,11,12,14]. In order to produce truly portable electronic devices, higher energy density batteries are required that are thus lighter and more compact. They constitute a significant proportion of the total mass and volume of such electronic devices.

In order to achieve higher energy densities, researchers have considered more reactive electrode materials, such as lithium and sodium, that exhibit higher electrode potentials and in turn higher cell voltages [13,15]. Higher cell voltages mean that fewer cells need to be joined in series to reach the desired battery voltage, which reduces the volume and mass of the battery and hence increases the energy density. Lithium and sodium are also considerably lighter than more traditional cathode materials, such as lead or cadmium, which further increases their energy density benefit. However, the highly reactive nature of lithium and sodium meant that conventional aqueous electrolytes could not be used. The main alternatives to aqueous electrolytes were a metal salt dissolved in an organic solvent, which gave rise to Li-Ion batteries, and a solid macromolecule or ceramic, which were the technologies that prompted the development Li-Ion Polymer [14] and 'ZEBRA' [13,15] batteries respectively (see Table 1). The latter term was derived from 'ZEolites applied to Battery Research Africa', which was a secretive collaborative project in the mid-1970s – during the 'apartheid' era - between the South African Council for Scientific and Industrial Research (CSIR) and the Anglo American Corporation of South Africa [16]. They are high-temperature electric batteries that use molten salts as an electrolyte.

Table 1 The principal materials utilised and charge/discharge cycle life assumed for each battery technology evaluated.

Battery Technologies	+ve Electrode	-ve Electrode	Electrolyte	Casing	Approximate Cycle Life
Lithium-Ion (LIB)	Lithium Cobalt Oxide ($LiCoO_2$)	Graphite	Lithium hexafluorophosphate ($LiPF_6$)	Steel	1500 cycles
Lithium-Ion polymer (LIP)	Lithium Cobalt Oxide ($LiCoO_2$)	Graphite	'Gel'	Steel Foil	400 cycles
ZEBRA - Sodium Nickel Chloride (NaNiCl)	Nickel Chloride ($NiCl_2$)	Sodium	Sodium chloroaluminate and Beta-alumina	Steel	1000 cycles
Nickel-Cadmium (Ni-Cd)	Nickel Oxide [NiO(OH)]	Cadmium	Potassium Hydroxide (KOH)	Steel	2000 cycles

1.3 The Issues Considered

Several ARBT have been appraised here, including Lithium-Ion batteries (LIB), Li-Ion Polymer (LIP) and Sodium Nickel Chloride (NaNiCl) [or 'ZEBRA'] batteries [6-15]. These are compared to the more mature Ni-Cd batteries. Specifications for the materials content of the batteries were taken from emerging, commercially available devices (as outlined in Table 1). An indicative energy technology assessment of such ARBTs was evaluated using energy, environmental, and economic appraisal techniques. It is 'indicative' in the sense of being a simplified evaluation and illustration of the performance of state-of-the-art rechargeable batteries. Nevertheless, such assessments provide a valuable evidence base for developers, policy makers, and other stakeholders. The energy analysis and environmental appraisal were conducted on a 'cradle-to-gate' life-cycle basis for each of the ABRTs: see Fig. 1. The suitability of these advanced rechargeable energy storage devices for different applications, such as electric vehicles (EV) [7,10], consumer electronics [14,15], load levelling, and stationary power storage, has also been assessed technically.

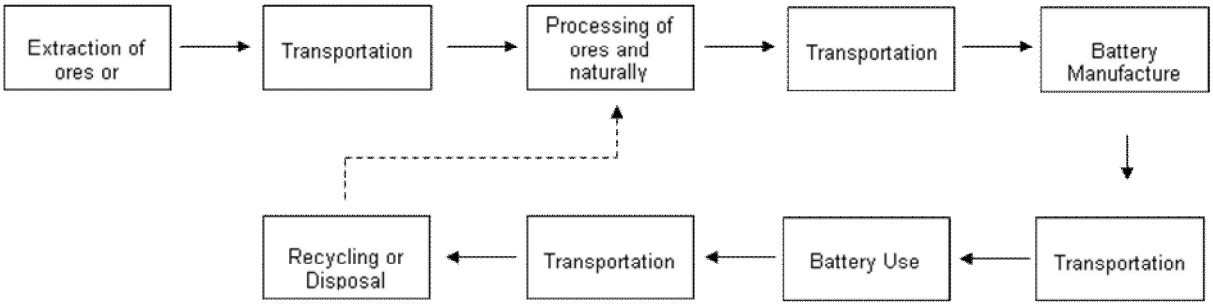

Fig. 1. The Advanced Rechargeable Battery Technology (ARBT) life-cycle.

2. ADVANCED RECHARGEABLE BATTERY TECHNOLOGIES

2.1 Li-Ion Batteries

Several different positive electrode materials for 'systems of choice' Li-Ion batteries have been trialled over the years, including Lithium Cobalt Oxide ($LiCoO_2$), Lithium nickel oxide ($LiNiO_2$) and Lithium Manganese Oxide ($LiMn_2O_4$) [9-12,14]. The most commonly used is $LiCoO_2$ because of the high voltage generated by cobalt with respect to Lithium. When a Li-Ion cell discharges, positively charged Li-Ions flow from the negative electrode to the positive $LiCoO_2$ electrode [8-9]. During charging, a current is passed through the cell in the opposite direction. The chemical reaction is then reversed and the Li-Ions return to the cathode. Early Li-Ion cells utilized a solid Lithium metal as the negative electrode. However, it proved too reactive and quickly formed an insulating 'passivating layer' that inhibited charge and discharge [7,9,11,12]. Consequently, a more stable graphite 'insertion' electrode that mimicked the behaviour of the $LiCoO_2$ electrode replaced the negative Lithium electrode (Table 1). Insertion electrodes permit the relatively small Lithium ions to flow into gaps in their material structure.

Current mass-market uses of Li-Ion cells are limited to applications that require very compact energy storage such as portable consumer electronics and heart pacemakers [14]. Attempts are being made to scale-up the technology for use in electric vehicles, airplanes and satellites. However, issues of safety, cost and lifetimes for Li-Ion cells have yet to be fully addressed in such applications. For example, in early January 2013, fires occurred on two Japanese-operated Boeing 787 *Dreamliners* (new, super-efficient passenger aircraft) linked to their Li-Ion batteries. In one case, batteries in the tail overheated and started a fire. A second aircraft had to make an emergency landing when the cockpit monitor indicated battery overheating. The US *Federal Aviation Administration* (FAA) subsequently ordered the *Dreamliner* fleet grounded until Boeing could confirm that its Li-Ion batteries were safe. In April 2013 the FAA announced that *Dreamliners* could return to limited service after design changes were made to their battery systems, although the exact cause of the original battery failures was still unknown. But a further problem arose with a Japanese Airlines Boeing 787 when one emitted smoke from the battery's protection exhaust in January 2014, while the aircraft was undergoing pre-flight maintenance, and it partially melted.

2.2 Li-Ion Polymer Batteries

Li-Ion Polymer cells utilize identical cell chemistry to Li-Ion cells. Early 'Li-polymer' cells developed in the late 1970s had a solid electrolyte and could therefore be manufactured at a thickness of only ~1mm [9,11,15]. This was achieved by stacking the components of the battery in a series of layers. They were more rugged, due to the absence of a liquid electrolyte, and there was no risk of explosion. Unfortunately, they suffered from poor conductivity and couldn't deliver the current bursts demanded by modern mobile electronic devices [15]. LIP batteries were consequently developed that featured the same stacked layer construction, but with the addition of a gel to the solid electrolyte (Table 1). This enabled the conductivity to be increased to close to Li-Ion levels in return for sacrificing some of the ruggedness and compactness [9,11,15].

The relatively benign nature of Li-Ion Polymer batteries has been one of their main attractions over recent years. When combined with their thin profile, which allows the battery to flex, LIP batteries have been considered for some of the more futuristic applications. These include sowing the batteries into coats as part of an inbuilt entertainment system. However, the high cost of LIP batteries, even compared to Li-Ion batteries, has meant they have struggled to penetrate mainstream markets.

2.3 ZEBRA Batteries

The development of ZEBRA cells in South Africa was originally focused on a liquid Sulphur anode incorporated into a porous 'zeolite structure', together with a Sodium cathode [6,7,16]. When it became clear that the Sulphur electrode was incapable of sustaining a realistic current density, the idea was dropped and the focus shifted towards a Nickel Chloride ($NiCl_2$) positive electrode. However, the name remained fixed, and the cell chemistry became known as ZEBRA batteries [7,8,16].

In common with other battery types, ZEBRA batteries function by facilitating the flow of Sodium Ions from the cathode to the anode upon discharge. The Sodium Ions then return to the negative electrode when the cell is charged. The cathode is Sodium metal, whilst the positive electrode is solid metal Chloride powder, normally $NiCl_2$, dissolved in an electrolyte [16]. Modern ZEBRA cells in fact feature two electrolytes: β-alumina and Sodium chloroaluminate (Table 1). The solid β-alumina ceramic acts a separator to prevent the positive and negative electrodes coming into contact and short-circuiting [6,7,16]. In contrast, the role of Sodium chloroaluminate is to make ionic contact between the β-alumina electrolyte and the solid anode [7,8,16]. Unfortunately, the β-alumina electrolyte requires temperatures of 250°C – 400°C to function properly and, as such, ZEBRA batteries form part of the 'high temperature' family of batteries [16]. Although this doesn't have any safety implications (since ZEBRA cells are not susceptible to thermal runaway) it does rule out applications in consumer electronics. However, ZEBRA cells have been utilized successfully in a number of electric vehicle projects, such as the 'Stingray' developed by the Santa Barbara Electric Transportation Institute (California, USA) in the early 1990s [16]. These buses were tested in San Francisco against diesel counterparts, and were found to exceed the diesel buses

in power when climbing hills. The San Francisco Municipal Transportation Agency subsequently ordered 25 for their transit system. Similarly, five EV buses powered by ZEBRA cells were tested in Lyon (France) in 2004, and found to be performing as well as their diesel equivalents.

1. MATERIALS AND METHODS

3.1 Energy Analysis

In order to determine the primary energy inputs needed to produce a given artefact or service, it is necessary to trace the flow of energy through the relevant industrial sector [18]. This is based on the First Law of Thermodynamics or the notion of an energy balance applied to the system. The system boundary should strictly encompass the energy resource in the ground (known as the 'cradle'). In the present analysis the downstream boundary is known as the 'gate' {hence, 'cradle-to-gate' [19]} - effectively taken as the point of electricity end-use: in the home, a road vehicle, by the commercial service provider, or in the factory. Consequently, it effectively accounts for all UK power sector primary energy use (and associated emissions). Energy analysis yields the whole-life or 'Gross Energy Requirement' (GER) of the product or service system [18,20,21,22]. Likewise, the sum of all primary energies required to yield one unit of delivered energy is known as the 'Energy Requirement of Energy' (ERE). Thus, the sum of all the outputs from this system multiplied by their individual energy requirements must be equal to the sum of inputs multiplied by their individual requirements. The process consequently implies the identification of feedback loops, such as the indirect or 'embodied', energy requirements for materials and capital inputs. This procedure is indicated schematically in Fig. 2. Several differing methods of EA have been developed, the most significant being statistical analysis, Input-Output (I-O) analysis, process analysis (or energy 'flow charting'), and hybrid analysis [18,20,21,22].

A number of energy 'figures of merit' were used to compare the battery technologies. Energy density can be related to the size (volumetric energy density; Wh/l) and weight (gravimetric energy density; Wh/kg – sometimes termed 'specific energy') of the battery technology. These parameters are crucial for applications such as portable electronic equipment [9,11,12,14], where the consumers see more compact and lightweight devices as highly desirable. Even when the size and weight of the battery aren't of primary importance, high energy densities are preferable since they reduce the energy storage footprint and minimize logistical difficulties. In contrast, the gravimetric power density (W/kg) is a measure of how quickly a battery can be discharged [8]. This parameter is important for applications such as electric vehicles [8,10], which require sudden current surges for acceleration and hill climbing. Once again it is preferable to have a high power density regardless of the application. It means the battery is able to respond to unexpected surges in demand for current and as such introduces a greater degree of flexibility into the system. The energy and power density figures were taken straight from the relevant technical specifications. Finally, the '**P**roportion of **E**nergy **I**nputs that are **W**asted' (PEIW) is a measure of the proportion of energy inputs 'wasted' during production and transportation of the battery, and through energy inefficiencies in the battery itself. [Details of the way in which this parameter was estimated are given in Appendix A below.]

Using a single measure of energy wastage avoids unnecessary detail when comparing the technologies. The ‘wasted’ energy could be broken into several categories, such as energy required for production, energy losses through self-discharge, energy losses through maintaining the battery at its operating temperature, etc. However, this would merely distract from the overall measure, and may even confuse readers who are unfamiliar with battery terminology.

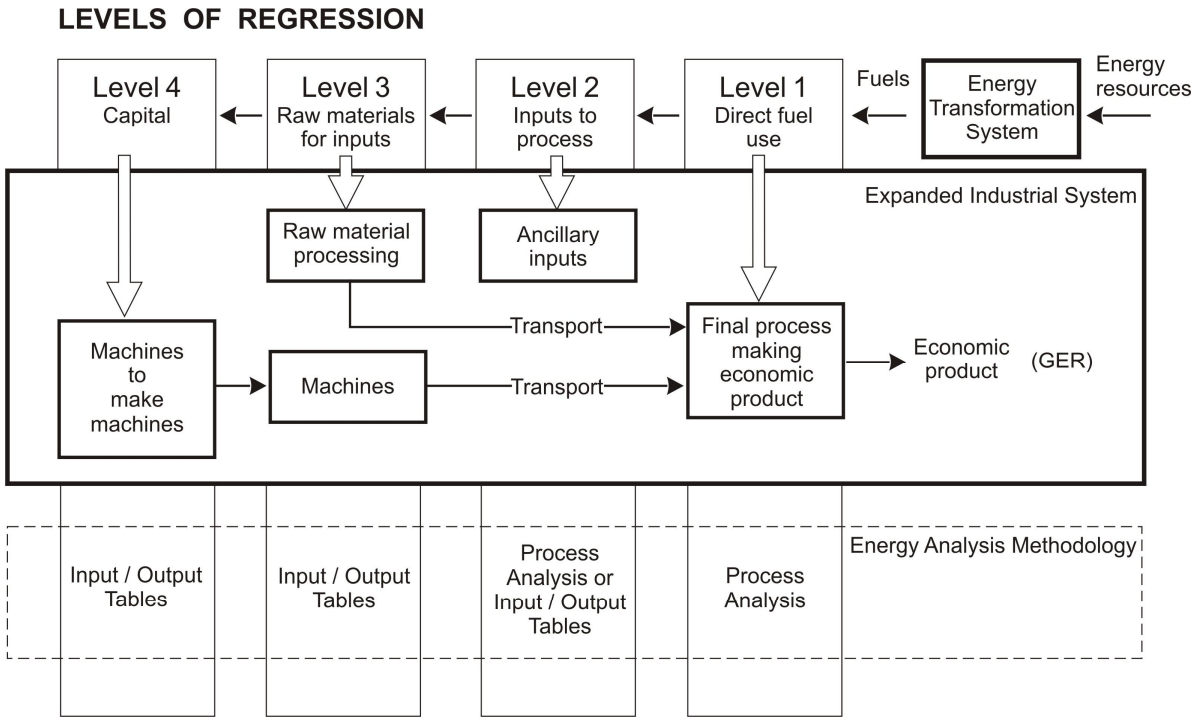

Fig. 2. Schematic representation of the energy analysis process. (Source: Allen *et al.* [22]; adapted from Slesser [21]).

1.2 Environmental Life-cycle Assessment (LCA)

Energy analysis preceded LCA and as such they share much of the same fundamental methodology. In order to evaluate the environmental consequences of a product or activity the impact resulting from each stage of its life-cycle must be considered. This led to the development of ecotoxicology, or a study of the harmful effects of releasing chemicals into the environment, and a range of analytical techniques that now come under the 'umbrella' of life-cycle assessment. The aim of the LCA is often to identify opportunities for environmental improvement [22] by detecting the areas with the most significant impacts. In a full LCA, the energy and materials used, and pollutants or wastes released into the environment as a consequence of a product or activity are quantified over the whole life-cycle, “from cradle-to-grave” [23,24]. Here the downstream boundary is again effectively taken as the point of electricity end-use: in the home, a road vehicle, by the commercial service provider, or in the factory. An LCA is often geographically diverse; that is, the energy and material inputs to a product may be drawn from any continent or geo-political region of the world.

There are four main stages of an LCA [25,26] which follow a logical sequence of goal definition and scoping (outlining aims, methodology and boundary conditions), inventory analysis (data collection - determining inputs and outputs of materials, fuels, and process emissions), impact assessment (determination of the life-cycle environmental impacts for the pre-determined inventory), and recommendations for improvement: see Fig. 3. Gathering data for the life-cycle inventory (LCI) can be a time-consuming task, as many companies either see such data as confidential or simply do not have the sort of detailed records needed for a credible whole-life study. The impact assessment and interpretation stages are still undergoing refinement; although they have been codified in the ISO 14040-14044 standards (launched in 2000, but revised in 2006 [25,26]). The LCA stages as applied in the present study were:-

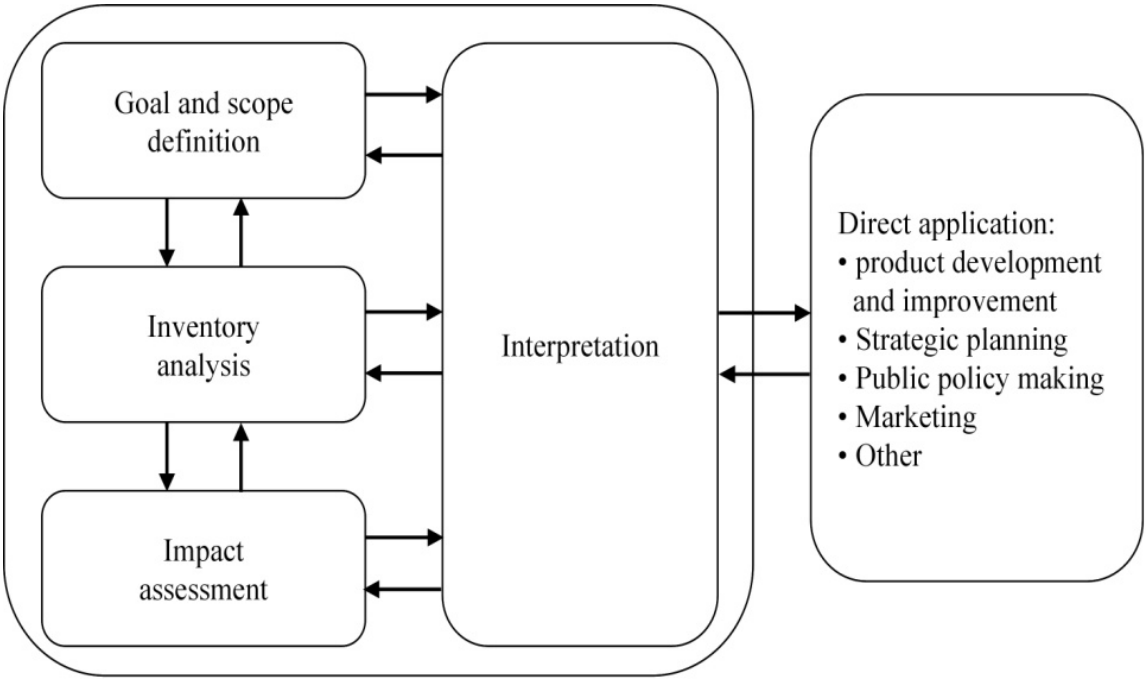

Fig. 3. The four main stages of environmental LCA (Source: Allen *et al.* [22]; adapted from ISO [25,26]).

Goal and Scope Definition: Here the issues to be examined are identified and the boundaries of the study clearly defined [25,26]. The goals of a LCA are usually to assess environmental impacts with respect to various known environmental problems such as global warming, acid rain and pollution of ground water. Consequently, **t**he first task was to specify the main stages in the life-cycle of a rechargeable battery as indicated in Fig. 1. The following goals were then established as: (i) the quantitative assessment of the contribution of the ARBT to global warming and acidification, or 'acid rain', resulting from CO_2 and SO_2 emissions respectively; and (ii) qualitative appraisal of the impact of ARBT arising from acid mine drainage and the emissions of metals and other particulate matter into the environment.

Inventory Analysis: This is the data gathering stage of an LCA study [25,26]. Data was gathered methodically for each stage in a battery's life-cycle in turn. However, the scarcity of the data meant it proved to be a challenging and time consuming process. The data-gathering

phase focused on two main sources: archival journal articles (e.g., [27-36]), as well as 'grey' literature from the Internet [35,36]. LIB and LIP batteries were treated as a single technology during the present LCA study, due to their inherent similarity of these technologies in terms of their materials content. The data for CO_2 and SO_2 emissions was limited to the extraction of raw materials, processing of raw materials, and transportation stages of the life-cycle (see again Fig. 1). It was assumed that the ARBT were produced wholly from virgin materials. Furthermore, the data for CO_2 and SO_2 production was limited to the metallic components of each battery, because the relevant data for other material components in the batteries was not readily available in sufficient detail. In cases where more than one extraction or processing technique existed, the data from the most widely exploited process was utilised in the calculations. There are no process emissions during the ARBT use phase, and no reliable data was available for emissions during manufacture. In addition, the emissions during recycling were assumed to be negligible. Throughout the inventory analysis care was taken to ensure that the data was consistent. For example, all of the LCA data for the production of Steel, Zinc and Nickel was obtained for processes that represented best practice technologies which minimise SO_2 emissions. Since these technologies reduce SO_2 emissions by approximately 90%, this was crucial to obtain consistency.

Impact Assessment: This phase normally consists of three sub-stages: 'Classification', 'Characterisation' and 'Valuation' [25,26]. The *Classification* sub-stage is where the data is split into the relevant categories, e.g., greenhouse gases emissions, emissions to water, etc., of the impact assessment occurred naturally as part of the data gathering. In the *Characterisation* stage of the impact assessment applied here the only emissions that were quantified in the current LCA study were the CO_2 and SO_2 emissions. Once an estimate has been made of the materials inventory for each battery type, then the mass of each component (kg or equivalent) is multiplied by its 'embodied' emissions per kg in order to yield the cradle-to-gate emissions (typically presented in terms of emissions per lifetime kWh). Environmental life-cycle data was readily available for the production of Steel, Nickel and Zinc [29,32,33]. The CO_2 and SO_2 emissions attributable to the production of Cobalt and Cadmium [29] were estimated on the basis of this data, because these materials are obtained from the same ores and processes as Nickel and Zinc respectively. The CO_2 emissions (kg CO_2) during transportation were calculated from the simple product of the distance travelled (km), litres of fuel consumed per km travelled, and the fuel conversion factor (kg CO_2/litre). It was assumed that the batteries were transported 3000km by articulated lorry (in common with the earlier energy analysis studies [32,33]). In the present LCA study there was no *Valuation* sub-stage to the impact assessment. This is a subjective process [25,26]; where the impacts are weighted in order to allow comparison. The raw CO_2 and SO_2 data provided sufficient information to draw conclusions regarding the impact of ABRT on global warming and acidification. Weighting would have only added complexity to the data without providing any new information.

Interpretation and Improvement Evaluation: This is the LCA stage (see Fig. 3) is where potential environmental improvements are identified [25,26] and graphs have been used here to illustrate the areas of significant impact of pollutant emissions associated with the various

ARBT. The findings of this analysis and related ARBT comparisons are presented in Section 4 below.

3.3 Economic or Financial Appraisal

Financial appraisal evaluates the costs and benefits of any project, programme, or technology in terms of outlays and receipts accrued by a private entity (household, firm…etc.) as measured through market prices [22]. It omits environmental 'externalities', or any costs or benefits that may occur beyond the firm or corporation. Financial appraisal uses the market rate of interest (net of inflation) as a lower bound, and therefore indicates the real return that would be earned on a private sector investment. An objective of the present study was therefore to complete an economic evaluation of the batteries over their life-cycle (and charge/discharge cycle lives). Ideally this would have entailed a life-cycle cost analysis, where data relating to the costs at each stage of the product life-cycle would be collected and collated to yield an overall cost for the ARBT. However, lack of available data meant the economic analysis was first based on current prices. Product 'experience curve' type analysis might subsequently be used to estimate future prices. 'Current prices' were obtained from in-depth Internet research. Care was taken to gather reliable, recently published data that gave a firm figure for the price rather than an estimate of future prices or a wide price range. Since no reliable data could be traced for Li-Ion Polymer batteries, the current price was based on two online 'e-zine' articles, which quoted a 10 % price premium for LIP batteries compared to LIB devices. Once the current prices for each technology (on roughly a 2010 baseline) had been established the data was normalized into $/kWh so that the values could be compared with ease. It was only possible to draw broad or 'indicative' findings from the current prices data, rather than precise figures.

There is a large body of literature concerning innovation and innovation theory [35]. A product life-cycle perspective of the innovation process is appropriate, as opposed to considering each innovation stage in isolation. The market penetration of a (successful) new technology typically varies in the manner of the hypothetical S-shape, or 'logistic', curve [36,37] shown in Fig. 4 [35]. Take-up of the technology begins slowly, then as commercial viability is reached production 'takes off', and finally the technology rapidly diffuses before gradually slowing down as the market saturates. The cost of production of a technology tends to reduce as production volumes increase; a phenomenon reflected by so-called technology *'learning curves'* or *'experience curves'* [35]. The causes of cost reduction vary, but can include 'learning by doing' improvements and economies of scale. It is therefore clear that higher costs for new technologies present a barrier to entry when competing with established technologies. This contributes to the 'lock-in' of incumbent technologies, and highlights the path dependence of development; both of which can discourage innovation [35]. In order to promote innovation and create a market for diverse technology options, these processes must be considered in the context of policy-making.

The product life-cycle curve of innovative technologies (including ARBT) follows closely the S-curve for generalised technological development: see again Fig. 4. The position of each battery technology on the product life-cycle curve was estimated in the present study using

historical and current sales data. Thus, the *Introductory* phase of the product life-cycle embraces '*Research, Development and Deployment*' (RD&D), and is where the ZEBRA battery technology is currently located. The *Growth* phase incorporates the 'Pre-commercial' and 'Supported commercial' (Fig.4), and this is where the LIP batteries are presently situated. It is characterised by a surge in sales as the product penetrates larger markets. The *Competitive* phase is that part of the S-curve (Fig.4) that represents the 'Fully commercial' market position, and is where the LIB is now located. This is often characterised by a combination of falling prices (due to intense competition) and continued sales growth as the popularity of the product grows. The *Mature* (or *Decline*) phase is characterised by falling sales and increased prices as the product becomes limited to small niche markets rather than mass markets. Ni-Cd batteries are moving into this position.

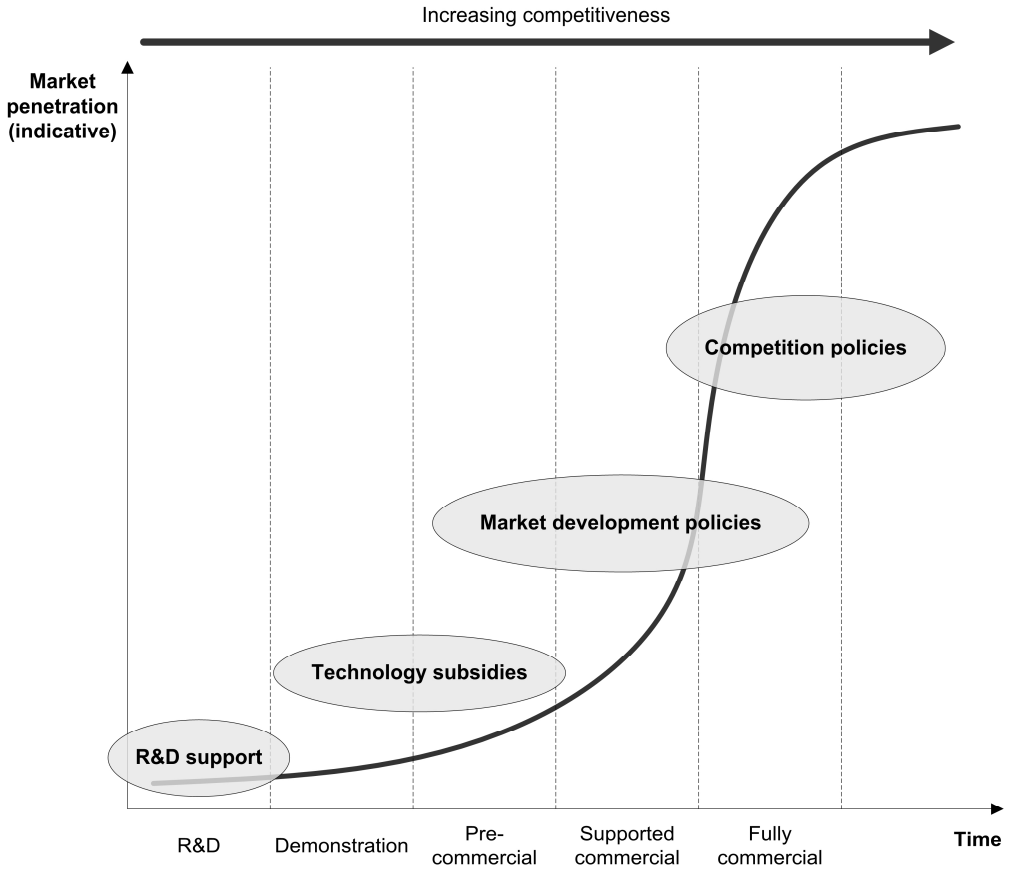

Fig. 4 S-curve of technology development and policy categories. (*Source:* Allen *et al.* [35]; adapted from Foxon *et al.* [36] and Midttun and Gautesen [37]).

4. RESULTS

4.1 Data Normalisation and Variability

The life-cycle accounting was performed on the basis of a normalisation process using the number of charge/discharge cycles for each battery type over the duration of their life (see the 'Approximate Cycle Life' data given in Table 1 above). ARBT are likely to age in different ways. For example, Lithium batteries often exhibit an abrupt end to their life. However, it is often difficult to obtain reliable, or independently verified, data from commercial companies. In addition, the technical performance and life of novel batteries will change over time; hopefully becoming more robust with practical usage. At the current state of development, the present results are intended to yield indicative performance information that will provide an initial evidence base for developers, policy makers, and other stakeholders. This will no doubt be refined as time moves forward.

Some of the data used in the energy analysis and LCA was only available as data ranges, not precise figures. In these circumstances, the middle value of the data range was utilized, which meant the results were the best estimate rather than a precise representation of reality.

4.2 Energy Performance

ARBT performance in terms of energy densities, power density, and PEIW are illustrated in Fig. 5-7 above. Li-Ion Polymer batteries clearly exhibited the best energy performance with the highest (gravimetric and volumetric) energy densities (Fig. 5), as well as power density (Fig. 6). The volumetric energy density of 266 Wh/l for LIP was particularly attractive, given that it is three times greater than Ni-Cd batteries, and almost twice that of Li-Ion and ZEBRA batteries. Richie [12] indicates specific energies for Li-Ion batteries of 140-150 Wh/kg using metal cans and 160-170 Wh/kg with light-weight packaging. These are in a similar range to the present results (see again Fig. 5). He argues [12] that further increases in gravimetric energy density for Lithium rechargeable batteries are possible to ~200-250 Wh/kg in the foreseeable future. These densities can be attributed to the highly reactive and lightweight Lithium Ions that form the basis of the technology, the absence of a liquid electrolyte, and the associated compact layered construction. The only weak energy characteristic of LIP batteries is that they 'waste' almost 45% of the total energy inputs over the lifetime of the battery. Whilst this is not a major issue at the moment, it may assume greater significance in the future depending on how attitudes towards wasting energy evolve. The problem could be addressed by improving the relatively poor **charge/discharge** cycle life of LIP batteries of just 500 cycles.

Li-Ion batteries exhibit a good all-round energy performance although, in contrast to LIP batteries, they do not excel in any one category. They outperform ZEBRA and Ni-Cd batteries, but by a smaller margin than LIP - typically 10-30% less. In common with Li-Ion Polymer batteries this performance is again largely due to the highly reactive, lightweight Lithium Ions that form the basis of the technology. If attitudes towards energy efficiency

harden, Li-Ion batteries' 'trump card' may prove to be the low PEIW compared to the other ARBT (Fig. 7) ZEBRA batteries exhibit higher energy and power densities (see Fig. 5 and 6) than the Ni-Cd comparator for similar reasons to Li-Ion batteries; namely their more reactive, lightweight cathode. However, whilst they outperform the more mature technologies zebra batteries do not compare well to LIB and LIP batteries. They exhibit lower energy densities than both Li-Ion technologies, and perform particularly badly in terms of power density, where the result is half and a third of LIB and LIP values respectively. The PEIW for ZEBRA batteries is also relatively high at 42% (Fig. 7). In a similar manner to Li-Ion polymer batteries this is mainly due to low **charge/discharge** cycle life, which results in the batteries being replaced more frequently and thus incurring a greater energy 'wastage' through production and transportation.

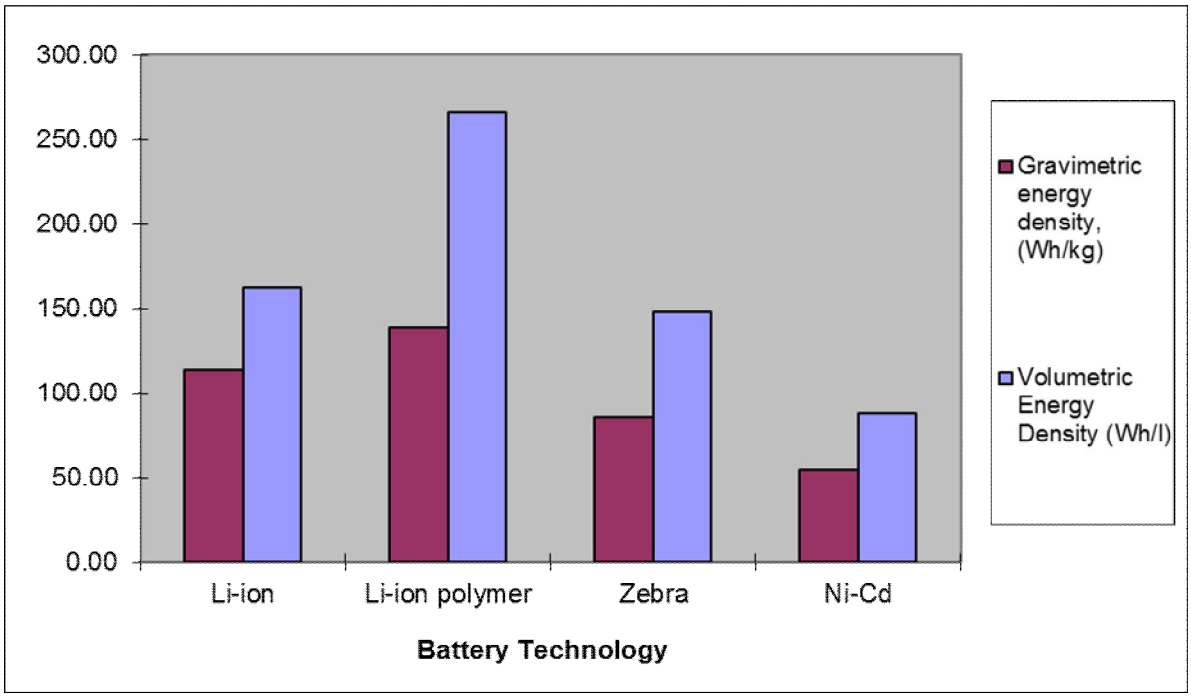

Fig. 5. Gravimetric and volumetric energy densities of rechargeable batteries.

4.3 Life-cycle Environmental Impacts

4.3.1 Greenhouse Gas Emissions

The cradle-to-gate life-cycle CO_2 emissions for Li-Ion and Li-Ion Polymer batteries were found to be 15 times lower than Ni-Cd batteries, and six times lower than ZEBRA batteries. This is shown in Fig. 8 and Table 2, where the separate contributions due to the battery manufacture as well as transport to the production plant. Table 2 also displays the total life-cycle CO_2 emissions. This indicates why LIB and LIP are the batteries of choice from a climate change perspective. It results from the relatively low proportion of metals in Li-Ion and Li-Ion polymer batteries, and crucially, the absence of the CO_2 intensive metals, such as nickel. The relatively high CO_2 emissions for Ni-Cd and ZEBRA batteries is a potential cause of concern, especially as supply chain and life-cycle impacts are once again becoming more high profile topics. In the short to medium term, it should not limit their use in larger-scale

applications, such as load levelling and EV, since the overall impact is relatively modest. For example, whilst a Ni-Cd battery produces almost 90 kg of CO_2 per kWh of capacity during its life-cycle (see again Table 2), this is paid back compared to the CO_2 emissions from a conventional petrol (or 'gasoline') combustion engine in just 15,700 km [assuming renewable (low or zero carbon) energy is used to charge the battery]. Since cars tend to complete well over 150,000 km during their lifetime this would represent a significant reduction in CO_2 emissions over the life-cycle of the car.

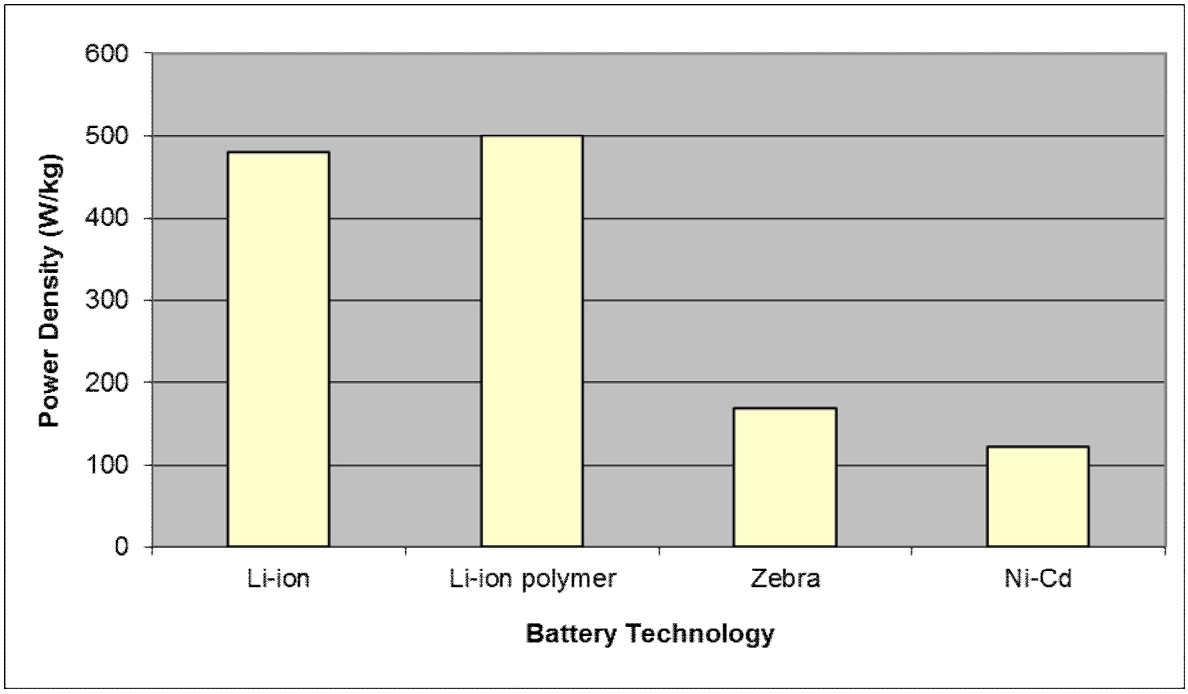

Fig. 6. Power densities of rechargeable batteries.

The CO_2 emissions associated with the fabrication and upstream transportation of raw materials for a 30kWh battery are depicted in Fig. 8 and Table 2. Cradle-to-gate life-cycle CO_2 emissions from Li-Ion and Li-Ion Polymer batteries are derived from operational or production and upstream (mainly transportation) emissions [19,38] in approximately equal measures. In contrast, for Ni-Cd and ZEBRA batteries the vast majority of life-cycle CO_2 emissions arise during the processing of the raw materials. During this process phase, the main CO_2 emissions emanate from the amount of energy used (or 'embodied' [18,19]) and the chemical reactions during the refining of the ores. After the ores have been 'beneficiated' at the mine, the main stages of processing are smelting (or 'roasting') and refining. Smelting removes the metal from its ore, whilst refining converts the metal oxide product of roasting to commercially pure metal (typically greater than 99% purity).

Since smelting, roasting and refining are all very energy-intensive activities, approximately 50% of CO_2 emissions from metal production are derived from the energy used, rather than the chemical reactions that occur during these processes [34]. Consequently, there is plenty of scope to reduce emissions of CO_2 by switching to renewable means of generating electricity or gas fuelled generation. Furthermore, CO_2 emissions over the life-cycle of the batteries

could be cut dramatically if they were manufactured from recycled materials [19]. On average batteries produced from recycled materials are 75% less energy intensive than batteries produced from virgin materials. Alternatively, the emissions of CO_2 could be sequestered via industrial CCS equipment.

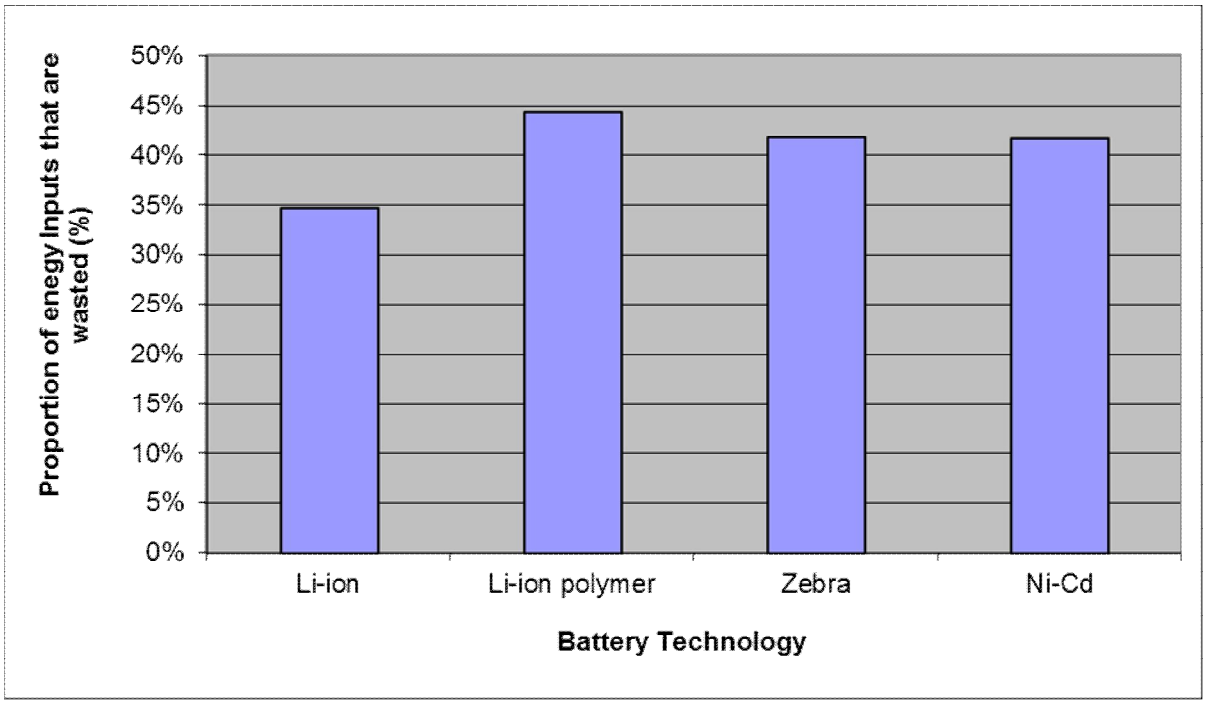

Fig. 7. '**P**roportion of **E**nergy **I**nputs that are **W**asted' (PEIW) in rechargeable batteries.

Table 2 Life-cycle carbon dioxide emissions from each battery technology evaluated.

Battery Technologies	**CO_2 During Production (kg/kWh)**	**CO_2 During Transportation (kg/kWh)**	**Total CO_2 Emissions (kg/kWh)**
Li-Ion & Li-Ion Polymer	2.6	2.8	5.4
ZEBRA	28.7	3.7	32.4
Ni-Cd	82.9	5.9	88.8

Note: Estimated values presented to an accuracy of three significant figures.

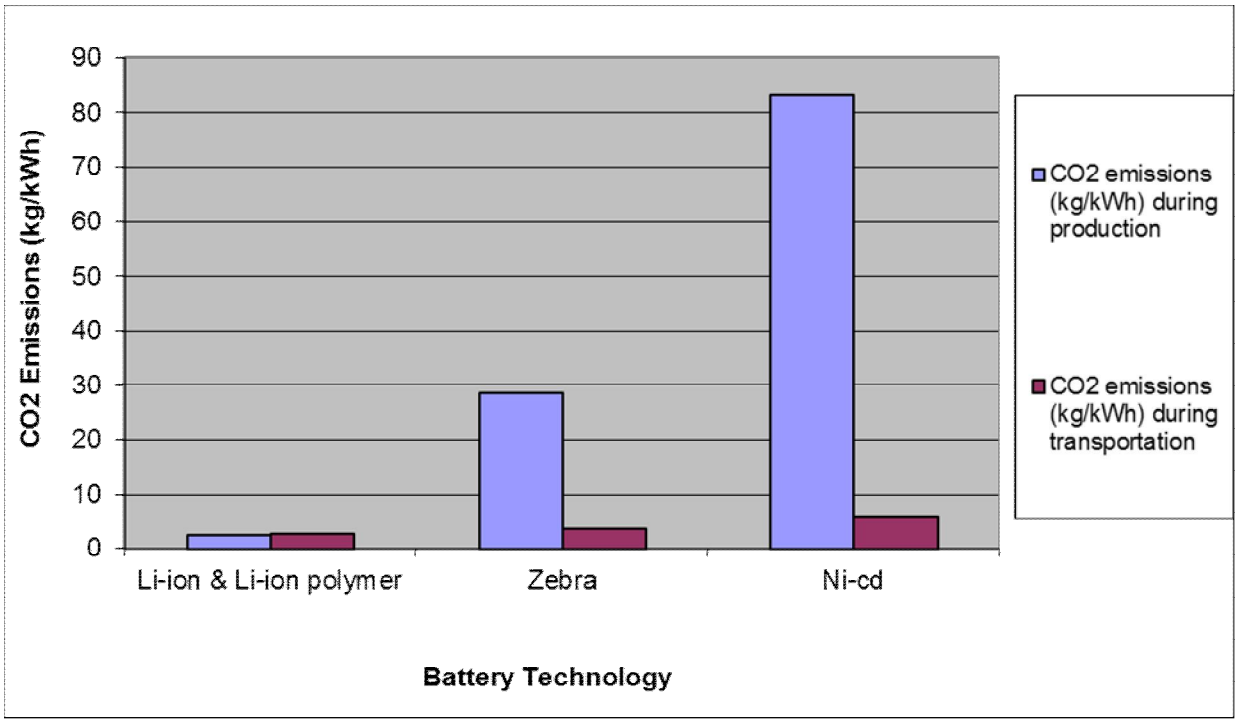

Fig. 8. Life-cycle carbon dioxide (CO_2) emissions associated with rechargeable batteries: Operational or processing emissions and those due to the transportation of raw materials.

The CO_2 emissions associated with the fabrication and upstream transportation of raw materials for a 30kWh battery are depicted in Fig. 8 and Table 2. Cradle-to-gate life-cycle CO_2 emissions from Li-Ion and Li-Ion Polymer batteries are derived from operational or production and upstream (mainly transportation) emissions [19,38] in approximately equal measures. In contrast, for Ni-Cd and ZEBRA batteries the vast majority of life-cycle CO_2 emissions arise during the processing of the raw materials. During this process phase, the main CO_2 emissions emanate from the amount of energy used (or 'embodied' [18,19]) and the chemical reactions during the refining of the ores. After the ores have been 'beneficiated' at the mine, the main stages of processing are smelting (or 'roasting') and refining. Smelting removes the metal from its ore, whilst refining converts the metal oxide product of roasting to commercially pure metal (typically greater than 99% purity).

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4.3.2 Acidification Emissions

In a similar manner to the CO_2 emissions, Li-Ion and Li-Ion Polymer batteries produce the lowest mass of SO_2 over their life-cycle. This is displayed in Fig. 9. The cradle-to-gate emissions are 3 times lower than both Ni-Cd and ZEBRA batteries, thus adding further weight to the body of evidence suggesting LIB and LIP are the batteries of choice from an environmental perspective. Compared to the CO_2 emissions, the magnitude of the SO_2 emissions are much smaller – only approximately 4 kg/kWh, compared to approximately 83 kg/kWh for the comparator Ni-Cd batteries. This is largely because the life-cycle data for the production of the metals was derived from studies [34] where the smelting and roasting plants are typically retrofitted with SO_2 reducing technology. This includes sulphuric acid plants that convert SO_2 into sulphuric acid, and flu gas desulphurization (FGD) plants that convert SO_2 into gypsum in order to produce, for example, plasterboard. Typically these technologies achieve a 90% reduction in SO_2 emissions, which is sufficient to meet the European Commission's '*Air Quality Framework Directive*' (96/62/EC). Consequently, provided all the smelting and roasting plants are fitted with SO_2-reducing technology, acidification will cease to be a significant environmental concern in terms of the production of batteries.

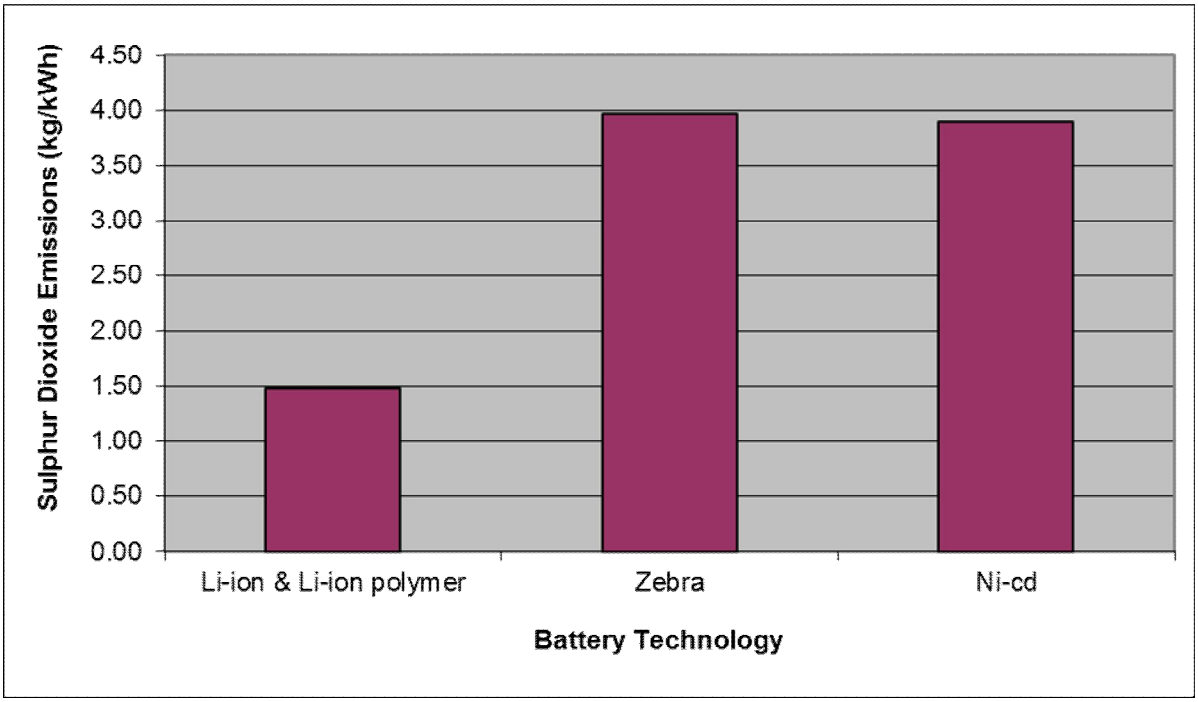

Fig. 9. Sulphur dioxide (SO_2) emissions associated with rechargeable batteries.

4.3.4 Particulate Matter Emissions

Unless preventative measures are put in place, 'particulate matter' (PM) is released into the atmosphere along with the gaseous products of combustion such as CO_2, SO_2 and NO_x when the metal ores are roasted or smelted. The PM emissions from smelting or roasting consist of microscopic particles (generally less than 10 microns in size, i.e., PM-10s) of unburnt hydrocarbons and heavy metals, such as Cadmium and Nickel amongst other things [38].

Numerous studies have linked PM-10s to aggravated cardiac and respiratory diseases such as asthma, bronchitis and emphysema and to various forms of heart disease [39]. These problems arise because of the size of the PM, which allows them to penetrate deep into the body. Children and the elderly, as well as people with respiratory disorders such as asthma, are particularly susceptible to health effects caused by PM-10 [39]. Furthermore, scientists now believe that there is no "threshold," or safe level, for exposure to PM. Li-Ion and Li-Ion Polymer batteries share a twin advantage over the other technologies considered in this study: a smaller mass of batteries is required to achieved the requisite capacity and each battery contains a significantly lower proportion of metal than Ni-Cd and to a lesser extent ZEBRA batteries. As a result, when the PM emissions are significant, the PM-10 emissions that may be attributed to LIB or LIP batteries are much lower than Ni-Cd and ZEBRA batteries.

4.3.5 Acid Mine Drainage and the Impact of Mining

Any raw material must be extracted from its naturally occurring environment before it can be processed to a usable form. The main raw materials in batteries are metals (see again Table 1) that are extracted from ores or minerals from the Earth's crust. All the metals relevant to ARBT, with the exception of Lithium, are derived in this manner. The latter is mainly extracted electrolytically from brine.

The mining process itself can have a significant impact on the local environment. The mine type, the local geology and the extent of government regulations largely determine the severity of this impact. Local residents often experience high levels of noise, dust and vibration, as well as problems associated with subsidence. In addition, local wildlife are frequently affected, especially during surface mining, when their habitats can be destroyed as the top-soil and vegetation are stripped away to access the mineral deposits. In addition, the visual impact of mines is often an issue where heavy machinery and large piles of 'tailings' and waste rock dominate the landscape [39]. Tailings are produced during the 'beneficiation' process to concentrate the ore, which typically increases the concentration of the mineral in the ore from less than 5% to 50 – 60%. The preferred method of beneficiation involves crushing the ore into fine particles before mixing it with water to create slurry. The slurry is then agitated with compressed air and a propeller that causes the mineral particles to stick to the bubbles and float to the surface where they can be collected. The remaining waste material is known as 'tailings'.

Acid Mine Drainage (AMD) is recognised as being the main environmental problem associated with mining [39]. If the mineral that has been mined contains sulphides, oxidation of the tailings and waste rock, it forms sulphuric acid that can dissolve heavy metals when aided the leaching action of rain and surface runoff. This combination of high acidity and heavy metals can then severely pollute nearby lakes, streams and rivers. Bridges can be corroded and aquatic life can be disseminated, as they are unable to tolerate the change in pH and high levels of poisonous metals.

The environmental impacts of mining metal ores are a cause for concern particularly for battery technologies, such as Ni-Cd and to a lesser extent ZEBRA batteries, which use large

proportions of mined metals (around 76% and 45% respectively [27]). The fact these battery technologies also require a relatively high mass of batteries compared to Li-Ion, and in turn a greater mass of metal, to achieve the requisite capacity is a notable disadvantage of Ni-Cd and zebra batteries. In contrast, Li-Ion batteries contain just 32% mined metal [27]. However, it should be noted that many of the environmental issues could be resolved, at least in part, through tighter regulations. For instance, the problem of acid mine drainage can be largely eliminated by burying the tailings and waste rock in an alkaline lined pit, such as a disused limestone quarry.

4.3.6 Recycling and Emissions from Land Fill Sites

The problems associated with mining metals for use in batteries (highlighted in Section 4.3.5 above) can be virtually eliminated through recycling. The technology exists to recycle all of the metals used in ARBT, although just 5% of rechargeable batteries are typically recycled in the UK: one of the worst records in Europe. However, recycling can be a profitable business since recycled metals can generally be produced using 75% less energy than virgin metals [19]. The onus is therefore on governments to introduce incentives to recycle batteries and accelerate efforts to end the 'disposable culture' that is still evident in Britain and elsewhere. In addition, governments need to encourage companies to invest in recycling plants, perhaps through grants, subsidies or tax breaks.

Emissions to the environment can also occur during the recycling or disposal phase of a battery's life-cycle (see again Fig. 1). A common way of disposing of refuse is landfilling – in the UK 60% of household waste was landfilled in 2010-2011 [http://www.defra.gov.uk/environment/waste/]. In fact, aside from smelting/roasting the main emissions associated with heavy metals occur when batteries are disposed of in landfill sites rather than being recycled. If the heavy metals come into contact with acids in the landfill site they can leach out and migrate into ground water and eventually drinking water supplies [39]. People and wildlife may, as a result, be exposed to elevated levels of heavy metals. In the short-term the problem of heavy metals from landfill sites entering drinking water can be prevented by lining new landfill sites with impermeable membranes [39]. However, this doesn't eliminate the problems associated with $LiPF_6$, Lithium, or KOH. Over the medium to long-term, a preferable solution remains to eliminate the problem at source by recycling batteries, rather than dumping them in land fill sites. Provided the correct systems, such as 'bag houses' and electrostatic precipitators, are in place the recycling of batteries has a minimal impact on the environment (since any PM emissions are captured). Whilst significant amounts of energy are used in this process, it represents a fraction of the energy required to extract virgin materials. Consequently, recycling reduces both CO_2 and SO_2 emissions.

It is possible to recycle all the metals used in batteries. In terms of the modern battery technologies, methodologies exist to recycle Ni-Cd and Li-Ion/Li-Ion Polymer batteries, and limited recycling programmes are in place. Likewise, ZEBRA cells have now been successfully recycled [40] at significant sizes to produce Nickel containing re-melt alloy, which is used in the stainless steel industry. The slag resulting from this pilot process was sold as a replacement for limestone used for road construction. The material value was then

found to cover the process cost of battery recycling and associated transportation. However, the fact more mature technologies, such as Ni-Cd, contain much higher levels of heavy metals compared to the ARBT is something of a 'double edged sword'. On the one hand there are many positive factors associated with the low metals demand for ABRT: there is less damage to the landscape, natural resources are conserved, and GHG and acidification emissions are lower. But, the lower proportion of metals also makes the recycling process financially unattractive to companies, since they stand to make less from the sales of the retrieved metals.

Apart from heavy metals, there are other problems associated with land filling with the disposal of batteries in landfill sites. The Lithium in Li-Ion and Li-Ion Polymer batteries can cause underground fires since it reacts vigorously and exothermically with water. The electrolyte (see Table 1) in LIB ($LiPF_6$) decomposes and produces highly toxic fluorine gas when it comes into contact with water. In addition, potassium hydroxide (KOH), the electrolyte from Ni-Cd batteries, is a strong alkaline and highly corrosive. KOH can be safely disposed of by neutralizing it with acid.

4.4 Economic Analysis

4.4.1 The ARBT Product Life-cycle

Li-Ion batteries are the most mature of the ARBT studied here, since they have just entered the competitive phase of their product life-cycle (see again Fig.4), and they are considered a mainstream technology in the consumer electronics sector. Their sales have grown strongly over the last decade. Similarly, Li-Ion Polymer batteries are entering the growth or pre-commercial phase. However, ZEBRA batteries are the least mature of these devices. They are still in the market demonstration stage, with trials for various automotive applications are still on-going and they have only achieved limited sales [16]. In stark contrast to the ARBT, the market for Ni-Cd batteries has been in moderate decline for some time. This was triggered by the emergence of LIB, which have eroded the position of Ni-Cd as the market leader in the high energy density market segment.

4.4.2 ARBT Prices

Li-Ion batteries were the cheapest of the technologies considered in this study (see Fig. 10). *Element Energy Ltd.* [41], following a recent study for the UK Government's independent Committee on Climate Change, suggest costs of <$250/kWh for consumer cells in comparison to the present estimates for LIB and LIP batteries of ~$210/kWh, against the Ni-Cd comparator at $240/kWh. This low price is partly a reflection of the 'first to market' advantage over the other ARBT, which meant that Li-Ion batteries entered mass production whilst the other technologies were still in development. The inevitable intense competition between suppliers then led to downward pressure on prices. Li-Ion batteries possess a 10% and 20% price advantage over LIP and Ni-Cd respectively (see Fig. 10). Despite this price differential appearing to be relatively insignificant, the 10% price difference between LIB and LIP has still proved decisive in stunting the growth of Li-Ion Polymer batteries.

ZEBRA batteries are about twice the price of Li-Ion ones. *Element Energy* [41] suggest costs of $400/kWh for automotive cells compared to the ZEBRA cell estimate here of $440/kWh (see again Fig. 10). ZEBRA batteries are presently one of the 'technologies of choice' for EV development work. Indeed, Galloway and Dustmann [40] argue that the low material cost of these devices suggest scope for a price of around $100/kWh over (an unspecified) time. However, their uncompetitive prices at the moment compared to LIB have had a relatively minor impact on the development of ZEBRA batteries, since the technologies are aimed at different markets. Li-Ion batteries have been developed for the portable electronics market, whilst ZEBRA batteries are primarily aimed at the EV or hybrid vehicle markets. However, it could be argued that research investment in ZEBRA batteries has been affected by the industry-wide consensus that LIB will be scaled-up in the future to cater for larger applications. The high prices for ZEBRA batteries can be attributed to the fact that they aren't yet in mass production and, as such, cannot benefit from the associated economies of scale and (learning curve) improvements in efficiency implied by the longer-term forecast of Galloway and Dustmann [40].

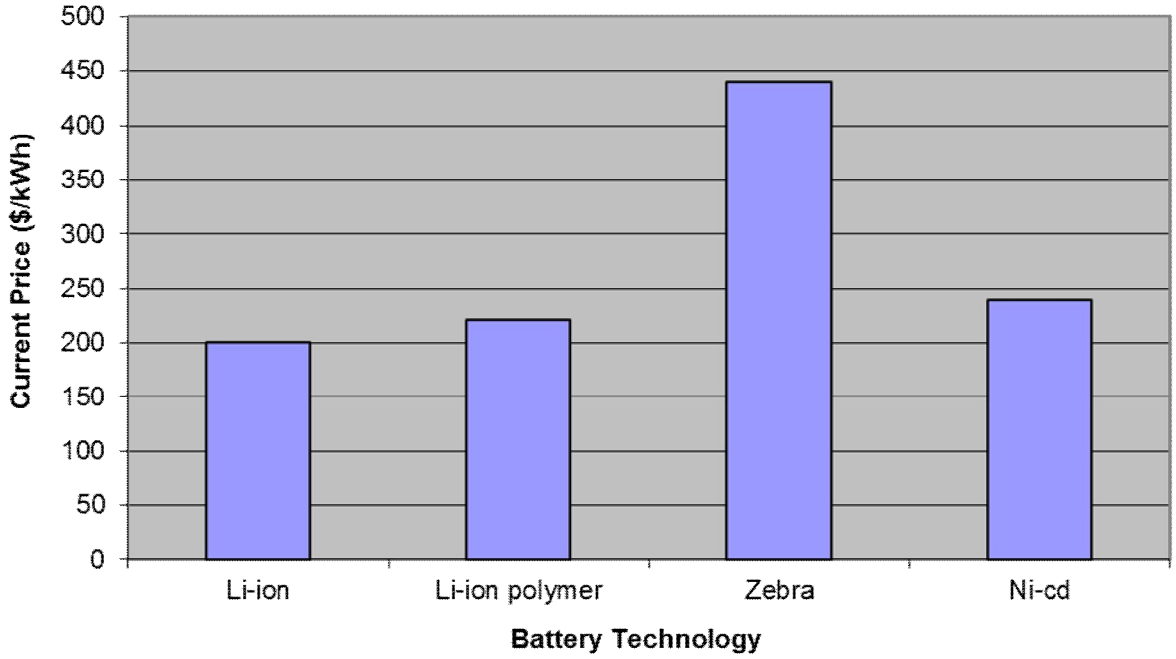

Fig. 10. Comparative prices of Advanced Rechargeable Battery Technologies

4.4 Technical Analysis

4.5.1 Battery Operating Temperatures

Li-Ion and Ni-Cd battery technologies examined in this study share very similar operating temperatures of around –20°C to +40°C. In contrast, the operation of ZEBRA batteries is independent of the ambient temperature. This is because, in order for the electrolyte to perform its function properly, the cells must be kept in the temperature range 250°C to 400°C. This represents a competitive advantage for ZEBRA batteries and will become more significant if the charge/discharge cycle lives of the ARBT converge in the future. Although the other battery technologies can operate in wide temperature ranges their service life is

impaired when the ambient temperature leaves the optimum 15ºC to 25ºC range [11]. For instance, if a Li-Ion or Li-Ion Polymer battery is stored at an ambient temperature of 35ºC, its charge/discharge cycle life is reduced by 45% [11]. Ni-Cd batteries aren't as badly affected, so whilst the impact is still noticeable they remain a sound option for high charge/discharge cycle applications even in temperature extremes. In fact, at the moment, the advantages of ZEBRA batteries are negated by their lower charge/discharge cycle lives. Nevertheless, ZEBRA batteries represent the best option at extreme temperatures. The exception is high charge/discharge cycle applications, when Ni-Cd may still represent the most favourable option (see Section 4.5.2 below).

4.5.2 Battery Cycle Life

In terms of their charge/discharge cycle life (see again Table 1 above), ARBT performed relatively poorly compared to Ni-Cd (~2000 cycles at operating temperatures between -20 to +45ºC). But Ni-Cd batteries have been around for a lot longer and subsequently benefited from prolonged investment over the RD&D phase of their product life-cycle (Fig. 4). However, the fact remains that only Li-Ion (1500 at -20 to +45ºC) has anything approaching the charge/discharge cycle life of Ni-Cd. Li-Ion Polymer has a particularly poor performance by any measure with a cycle life of just 400 charge/discharge cycles (again at -20 to +45ºC). ZEBRA batteries certainly don't currently excel in this area either. Their cycle life of 1000 charge/discharge cycles means that for high cycle applications the cost of the energy storage would effectively be double that of Ni-Cd. [The ZEBRA electrolyte operates at between 250 and 400ºC (as noted in Section 4.5.1 above).] Over time it would be fair to assume that the charge/discharge cycle life of all the ARBT would improve significantly as RD&D progresses. However, that doesn't change the fact that over the lifetime of the product, Ni-Cd batteries currently represent the cheapest option for high charge/discharge cycle applications of 1500 cycles or more. For low cycle applications the charge/discharge cycle life is largely irrelevant, and the choice of batteries would be determined by other factors.

4.5.3 Battery Safety

If the ARBT, or indeed any battery, is used in the correct manner they are essentially safe technologies. Safety only becomes an issue upon misuse. If the battery and cell casings are pierced, then the contents of the batteries can spill harmful or dangerous substances. The Lithium and Sodium from LIB, LIP and ZEBRA batteries are extremely flammable and heavy metals, such as cobalt and nickel, are toxic if ingested [11]. Ni-Cd batteries are also potentially dangerous, due to the toxic Cadmium and highly corrosive Potassium hydroxide (KOH) electrolyte (Table 1) [11]. Overall, in terms of release of materials following misuse there is little to choose between any of the ARBT evaluated here and Ni-Cd cells. However, the problems surrounding thermal runaway [42] means that LIB was the most dangerous of the ARBT considered.

Li-Ion Polymer batteries do not suffer from thermal runaway because they feature a gel polymer electrolyte [42] in contrast to the liquid $LiPF_6$ in Li-Ion batteries (see again Table 1). It occurs in LIB when they are accidentally over heated, which causes the $LiCoO_2$ cathode to react with the electrolyte before the reaction spirals out of control. In order to initiate this

reaction a temperature of 60°C is required, which would once again represent misuse of the battery. However, it should also be noted that thermal runaway is a rare occurrence even at elevated temperatures. In addition, steps are being taken to develop safer positive electrodes for the LIB [42]. Nevertheless, reference has already been made (see Section 2.1 above) to the thermal problems linked to Li-Ion batteries that were experienced by two Japanese-operated Boeing 787 *Dreamliners* passenger aircraft in early January 2013 and again in January 2014. The US FAA announced in the following April 2013 that *Dreamliners* could return to limited service after design changes were made to their battery systems, although the exact cause of the original battery failures was still unknown.

2. CONCLUDING REMARKS

An indicative technology assessment has been conducted on several 'Advanced Rechargeable Battery Technologies' (ARBT) [including Lithium-Ion batteries (LIB), Li-ion Polymer (LIP) and Sodium Nickel Chloride (NaNiCl) {or 'ZEBRA'} batteries] using energy, environmental, economic, and technical appraisal techniques. The energy and environmental performance of these batteries were evaluated on a 'cradle-to-gate' life-cycle basis (see Fig. 1). In concert, the suitability of ARBT for different applications, such as electric vehicles (EV), consumer electronics, load levelling, and stationary power storage, has been assessed. They have been compared to more mature Nickel-Cadmium (Ni-Cd) batteries in order to gain a sense of perspective regarding the performance of the ARBT. LIBs currently dominate the rechargeable battery market and are likely to continue to do so in the short-term in view of their excellent all-round performance, and firm grip on consumer electronics. However, in view of the competition from LIP batteries their long-term future is uncertain. Although, if safety concerns are overcome and costs fall significantly, there may be growth in the EV sector and to a lesser extent load-levelling, where Li-ion batteries can exploit their relatively high charge/discharge cycle life.

LIP batteries exhibited attractive values of gravimetric (or specific) energy, volumetric energy, and power densities (see Fig. 5-7). In the transport sector, *Element Energy Ltd.* [41] suggest a range of 100-180 Wh/kg in contrast to the estimates here of 80-130 Wh/kg (Fig. 5) against the Ni-Cd comparator of ~55 Wh/kg. LIB and LIP batteries also display low CO_2 and SO_2 emissions [see Fig. 8 (and Table 2) and Fig. 9 respectively], and are therefore environmentally attractive. Consequently, they are likely to dominate the consumer electronics market in the long-term, once mass production has become established, but may struggle to break into other sectors unless their charge/discharge cycle life and cost are improved significantly. *Element Energy* [41] suggest costs of <$250/kWh for consumer cells in comparison to the present estimates for LIB and LIP batteries of ~$210/kWh (see Fig. 10), and $400/kWh for automotive cells compared to the ZEBRA cell estimate here of $440/kWh against the Ni-Cd comparator at $240/kWh (see again Fig. 10). ZEBRA batteries are presently one of the technologies of choice for EV development work. Indeed, Galloway and Dustmann [40] argued that the low material cost of these devices suggest scope for a price of $100/kWh over (an unspecified) time. Nevertheless, compared to other ARBT, such batteries only represents an incremental step forward in terms of energy and environmental performance.

There has been some concern over recent years about potential shortages of some critical materials at a world level. It has been speculated, for example, that the availability of Lithium reserves may fall below that required to meet the future demand for Li-Ion batteries, which would be needed to enable the electrification of road transport vehicles [45]. Likewise, 'Rare Earth Elements' (REE) are a group of minerals which are important for low carbon energy technologies. They are not actually rare in terms of their abundance [46], but the number and location of mines are restricted due, in part, to economic considerations. Rare earth batteries and magnets are key elements of hybrid vehicles and gearless wind turbines, and phosphors are critical in energy saving lighting. Current REE reserves stand at about 110 million tonnes with around half in the People's Republic of China (PRC), although other countries like the USA, Commonwealth of Independent States (CIS) [the former Soviet Republics], and Australia hold substantial reserves [46]. Production in China dominates the market, with ~97% of the global total, and this will remain so until new mines are developed. The PRC has limited its export of REE in order to give preference to the export of manufactured products. Diversity of the global supply chain is therefore a crucial issue moving forward. It is likely that supply constraints will become less critical in the medium to long-term as more mines come into operation [46], and thus further reserves become available. Such constraints could be eased by reducing the amount of material required per application, or changing the technology altogether. Lithium-ion batteries, for example, are already a viable replacement for nickel-metal-hydride units in hybrid vehicles, although they could also be resource-constrained [45] as indicated above. REE are not currently recycled, either pre or post-use. There are processes available that could be utilised for this purpose, although they don't currently appear to be viable options [46].

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APPENDIX A. Estimating the 'Proportion of Energy Inputs that are Wasted' (PEIW)

The methodology that was employed in the present study to determine the PEIW over each battery's life-cycle is outlined below. It was adapted from a similar approach developed by Rydh [43] for batteries, and subsequently employed by Rydh and Sanden [32,33] in specific connection with batteries for solar photovoltaic systems. The first step in the process was to calculate the mass (M) of the batteries from the gravimetric energy density (E_{grav}) and the capacity (C), which was assumed to be 30kWh:

$$Mass\ (M) = \frac{E_{grav}}{C}$$

The electrical energy input over the lifetime of the battery (E_i) was then established from the capacity (C) and the maximum number of cycles (N):

$$Electrical\ Energy\ Input\ (E_i) = C \times 3600 \times N$$

The total electrical energy output E_o was calculated by multiplying the electrical energy input by the discharge factor (D), which was 0.8 in this study. It was important to differentiate between the electrical energy input and electrical energy output because in practice a battery is rarely fully discharged. A full discharge can cause irreparable damage to the battery so the depth of discharge is usually limited to 80% of the capacity, hence the discharge factor of 0.8.

$$Electrical\ Energy\ Output\ (E_o) = E_i \times D$$

Next, the total energy for production ($E_{P,pf}$) of each kg of battery (in fossil fuel 'energy currency') was calculated by summing the energy required to extract/process the raw materials ($E_{pr/ex}$) and the energy required to manufacture (E_{man}) the batteries.

$$Total\ Energy\ for\ Battery\ \text{Pro}duction\ (E_{P,pf}) = E_{pr/ex} + E_{man}$$

The Li-Ion, Li-Ion Polymer and Ni-Cd data for this calculation were taken from Rydh [43]. In contrast, the values for the ZEBRA battery were obtained in a rather more complex manner since no data was available for either the energy to extract and process the raw materials or the energy required to manufacture the batteries. The energy required to extract and process the raw materials was calculated from the breakdown of materials utilised to manufacture the battery, and the energy required to extract and process each individual material. The data for

the energy to manufacture the ZEBRA batteries was again extracted obtained from Rydh [43] by assuming the value was the same as that for Sodium Sulphur (NaS) batteries. They are a very similar battery technology to ZEBRA batteries; both in terms of materials and manufacturing techniques.

The next stage was to convert the total energy for production from primary fuel 'energy currency' into electricity 'energy currency'. The need for this process arose from the fact that electricity production from fossil fuels is only 35% efficient [1]. As such, comparing the electrical energy inputs to the battery with the primary energy required to extract and process the raw materials would not be comparing 'like with like'. The choice of electricity as the energy 'currency' mirrored the methodology adopted by Rydh [43]. The conversion process was completed using the following formula:

$$Total\ Energy\ for\ Battery\ \mathrm{Pr}oduction\ (E_{P,el}) = E_{P,pf} \times 0.35$$

In common with Rydh [43] in order to calculate the energy required to transport the batteries per kg of device ($E_{T,pf}$), it was assumed the batteries were transported a distance (L) by lorry from the factory to the point of use. It was also assumed that the journey was completed twice since the lorry would have to return to its country of origin. During the journey the lorry expended a given amount of energy per km (e_{truck}).

$$Total\ Energy\ to\ Transport\ Batteries\ (E_{T,pf}) = 2Le_{truck}$$

Once again the result was converted into electricity currency:

$$Total\ Energy\ to\ Transport\ Batteries\ (E_{T,el}) = E_{T,pf} \times 0.35$$

The total energy used to produce and transport the batteries ($E_{P\&T}$) was then calculated using the following formula:

$$Total\ Energy\ to\ \mathrm{Pr}oduce\ and\ Transport\ Batteries\ (E_{P\&T}) = (E_{P,el} + E_{T,el}) \times M$$

The energy loss (E_{loss}) in the batteries themselves was calculated using energy efficiency figures for each battery technology. The figures for Li-Ion, Li-Ion Polymer and Ni-Cd batteries were taken from Rydh [43], whilst the value for ZEBRA batteries was derived from a separate study by Rantik [44]. Energy inefficiencies (ρ) in LIB, LIP and Ni-Cd batteries arise due to self-discharge. In contrast, the energy inefficiency in ZEBRA batteries arises from need to maintain the electrolyte at its elevated operating temperature of 250 to 400^{o}C.

$$Energy\ Loss\ (E_{loss}) = E_i \times (1 - \rho)$$

Next, the total energy wasted (E_W) during the lifetime of the battery was calculated using:

$$Total\ Energy\ Wasted\ (E_W) = E_{P\&T} + E_{loss}$$

The total energy inputs over the lifetime of the battery ($E_{i,TOT}$) was then calculated using:

$$Total\ Energy\ Inputs\ (E_{i,TOT}) = E_i + E_W$$

Finally, the PEIW was calculated using the following formula:

$$PEIW = \left(\frac{E_W}{E_{i,TOT}} \right) \times 100$$

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NOMENCLATURE

Abbreviations

ARBT	**A**dvanced **R**echargeable **B**attery **T**echnologies
CCS	Carbon capture and storage (facilities)

CO_2	Carbon dioxide
defra	UK Department of Environment, Farming and Rural Affairs
GHG	Greenhouse gas emissions
IPCC	**I**ntergovernmental **P**anel on **C**limate **C**hange
ISO	**I**nternational **O**rganization for **S**tandardization
KOH	Potassium hydroxide
$LiCoO_2$	Lithium cobalt oxide
Li-Ion	Lithium-Ion battery (LIB)
Li-Ion Polymer	Lithium-Ion polymer (LIP) battery
$LiPF_6$	Lithium hexafluorophosphate
LCA	(Environmental) life cycle assessment
NaNiCl	Sodium nickel chloride
NaS	Sodium-sulphur battery
Ni-Cd	Nickel-cadmium battery
$NiCl_2$	Nickel chloride
NiO(OH)	Nickel oxide
PEIW	**P**roportion of **E**nergy **I**nputs that are **W**asted
PM	Particulate matter
SO_2	Sulphur dioxide
USA	United States of America
ZEBRA	**ZE**olite **B**attery **R**esearch **A**frica (high-temperature electric batteries that use molten salts as an electrolyte)